

Preparation and X-Ray Crystal Structure of Bis(pyridinium)- μ -Dichloro- μ -oxo-tetrachlorodiantimonate(III); a Discrete Antimony(III) Oxychloro-anion

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Summary Partial hydrolysis of the polymeric $(\text{pyH})_3\text{Sb}_2\text{Cl}_9$ (py = pyridine) in ethanol leads to $(\text{pyH})_2\text{Sb}_2\text{OCl}_6$ which is shown by X-ray crystallography to contain a discrete oxychloroanion of antimony(III) consisting of two octahedral $:\text{SbOCl}_4$ units sharing a face.

ONE of the major structural principles in the chemistry of anionic halogenoantimonates is the formation, depending on the stereochemical activity or otherwise of the lone pair of electrons, of either pseudo-octahedral $:\text{SbX}_6$ or octahedral SbX_6 basic units. With chlorine this often leads to infinite structures¹ in which adjacent octahedra share, at the most, an edge, while face sharing between two octahedra and the formation of discrete dimers is possible with the heavier halogens.² Neutral antimony(III) oxide chlorides invariably have infinite polymeric structures.³ We report here the preparation and crystal structure of an anionic antimony(III) oxide chloride which has a discrete dimeric structure resulting from the sharing of a common face between two pseudo-octahedral units. The triple bridge, rather surprisingly, involves one oxygen and two chlorine atoms.

Tris(pyridinium) nonachlorodiantimonate, prepared by the reaction of SbCl_3 with an excess of pyridinium chloride in ethanol has a polymeric, ribbon-type structure, as expected from the principles mentioned above, and can be recrystallised unchanged from dry ethanol.⁴ In the presence of water, crystallisation from ethanol gives a partially hydrolysed product, identified by microanalysis (C, H, N, and Cl) and i.r. spectroscopy [515s , $\nu(\text{Sb}-\text{O})$; 285 cm^{-1} , $\nu(\text{Sb}-\text{Cl})$] as $(\text{pyH})_2\text{Sb}_2\text{OCl}_6$ (py = pyridine).

Crystal data: monoclinic, space group $P2_1/c$, $a = 8.816(5)$, $b = 8.615(5)$, $c = 26.802(5)$ Å, $\beta = 104.63(5)^\circ$. The structure was solved by Patterson and Fourier methods using data for 2686 observed reflections and has been refined with anisotropic thermal parameters by full-matrix least-squares methods to R 7.2%. The anion structure is shown in the Figure and selected molecular parameters are included in the caption.†

The structure is based on two $:\text{SbOCl}_4$ pseudo-octahedral units which share the $\text{O}(1)-\text{Cl}(5)-\text{Cl}(6)$ face. The lone pair of electrons in each case occupies the sixth octahedral position which is *trans* to the bridging oxygen atom. Bonds to the terminal chlorine atoms (mean, 2.443 Å) are of normal length and are substantially shorter than those involved in bridging (mean, 2.886 Å). Bridging is asymmetrical at $\text{Cl}(6)$ but both $\text{Cl}(5)$ and $\text{O}(1)$ form symmetrical bonds with the angle at the latter being 119.5° . The $\text{Sb}-\text{O}$ distances fall

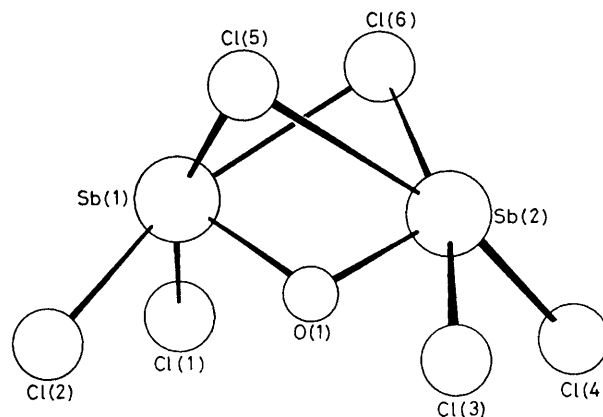


FIGURE. Structure of the $\text{Sb}_2\text{OCl}_6^{2-}$ anion: $\text{Sb}(1)-\text{Cl}(1)$ 2.437(3); $\text{Sb}(1)-\text{Cl}(2)$ 2.483(3); $\text{Sb}(2)-\text{Cl}(3)$ 2.419(4); $\text{Sb}(2)-\text{Cl}(4)$ 2.434(3); $\text{Sb}(1)-\text{Cl}(5)$ 2.878(4); $\text{Sb}(2)-\text{Cl}(5)$ 2.884(4); $\text{Sb}(1)-\text{Cl}(6)$ 2.832(4); $\text{Sb}(2)-\text{Cl}(6)$ 2.952(4); $\text{Sb}(1)-\text{O}(1)$ 1.948(8); $\text{Sb}(2)-\text{O}(1)$ 1.949(8) Å; $\angle \text{Cl}(1)-\text{Sb}(1)-\text{Cl}(2)$ 89.8; $\text{Cl}(1)-\text{Sb}(1)-\text{O}(1)$ 87.6; $\text{Cl}(2)-\text{Sb}(1)-\text{O}(1)$ 87.4; $\text{Cl}(5)-\text{Sb}(1)-\text{Cl}(6)$ 80.0; $\text{Cl}(3)-\text{Sb}(2)-\text{Cl}(4)$ 90.0; $\text{Cl}(3)-\text{Sb}(2)-\text{O}(1)$ 89.7; $\text{Cl}(4)-\text{Sb}(2)-\text{O}(1)$ 89.5; $\text{Cl}(5)-\text{Sb}(2)-\text{Cl}(6)$ 78.0; $\text{Sb}(1)-\text{Cl}(5)-\text{Sb}(2)$ 71.5; $\text{Sb}(1)-\text{Cl}(6)-\text{Sb}(2)$ 71.2; $\text{Sb}(1)-\text{O}(1)-\text{Sb}(2)$ 119.5°.

at the low end of the range of values found in previous structures and may contain a weak π -component.

Minimization of the non-bonded interactions between the two sets of terminal chlorine atoms requires that the $\text{Sb}-\text{O}-\text{Sb}$ plane bisects the $\text{Cl}(1)-\text{Sb}(1)-\text{Cl}(2)$ and $\text{Cl}(3)-\text{Sb}(2)-\text{Cl}(4)$ angles giving overall C_{2v} symmetry to the $\text{Cl}_2\text{SbOSbCl}_2$ skeleton. Of the remaining octahedral sites, only those *trans* to the oxygen atoms are electrostatically acceptable for the antimony lone pairs and the structure is completed by the formation of two chlorine bridges between the remaining octahedral positions. With an angle of *ca.* 120° at the oxygen atom, the $\text{Sb}(1) \dots \text{Sb}(2)$ separation falls to 3.37 Å, a value well within the van der Waals' distance (4.4 Å), and to complete the triple bridge the angles at the chlorine atoms are reduced to *ca.* 71.3° . At this stage, there seems to be no obvious reason for the preferential stabilisation of a discrete dimeric structure in this antimony(III)-chlorine system rather than the more characteristic polymeric structure.

The overall molecular structure is completed by two different types of weak interaction between the dimer units, in addition to hydrogen bonds between the pyridinium

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

cations and O(1) (2.68 Å) and Cl(6) (3.32 Å). The first contact between Sb(1) and a symmetry-related Cl(2) atom at 3.49 Å is very weak and leads to chains of anions parallel to the *b*-axis. The second between Sb(2) and a symmetry-related Sb(2) atom is at 3.81 Å and, most unusually, this is the only contact involving this atom.

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¹ See *e.g.* S. K. Porter and R. A. Jacobson, *J. Chem. Soc. (A)*, 1970, 1356; K. Kihara and T. Sudo, *Acta Cryst.*, 1974, **B30**, 1088.

² C. R. Hubbard and R. A. Jacobson, *Inorg. Chem.*, 1972, **11**, 2247; B. Chabot and E. Parthé, *Acta Cryst.*, 1978, **B34**, 645.

³ C. Sarnstrand, *Acta Cryst.*, 1978, **B34**, 2402; F. Sgarlata, *Period. Mineral.*, 1970, **A39**, 315.

⁴ M. Hall and D. B. Sowerby, unpublished observations.